

Speciated Monoterpene Emissions
and their Contribution to the Formation of
Secondary Organic Aerosols:
A Preliminary Study

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Introduction

Emissions of volatile organic compounds (VOC) from vegetation play an important role in the chemistry of the atmosphere due to the magnitude of biogenic VOC emissions and their reactivity with other trace atmospheric constituents¹. VOCs impact the oxidizing capacity of the atmosphere mainly through cycling of HOx and NOx radicals and tropospheric O₃ production. Monoterpenes are a class of VOC that can contribute significantly to both regional photochemical activity and secondary organic aerosol (SOA) formation². SOAs play an important role in global climate by absorbing or scattering radiation, and in serving as cloud condensation nuclei³. Additionally, these sub-micron sized aerosols fall under the PM 2.5 category (particulate matter less than 2.5 micron diameter), which are regulated at the state and federal level because they decrease visibility and threaten human respiratory health. However, the fraction of PM 2.5 that is SOA formed from monoterpenes is not understood. Accurate in-situ measurements of monoterpene emissions are crucial for our understanding of their effects on tropospheric chemistry and aerosol formation.

Monoterpenes are emitted by many families of flowering plants and by all conifers⁴. Thus, coniferous ecosystems have a tremendous potential for monoterpene emissions⁵. Their C-C double bonds allow for the high reactivity of terpenes with the nitrate radical, OH, and O₃. Many laboratory studies have shown that some products of these reactions partition into the aerosol phase under atmospheric conditions^{6,7,8}. These studies have focused mainly on α - and β -pinene, the two most commonly emitted terpene species. However, fourteen different species are commonly observed in the U.S., and their emissions exhibit high regional variability⁹. These individual terpene species differ in their oxidation rates, reaction products, and aerosol yields^{7,8,9}. Previous in situ measurements of terpenes have determined mixing ratios and fluxes of a limited number of terpene species¹⁰. However, because emissions of monoterpene species exhibit high regional variability, measurements of a limited number of species may not accurately represent the impact of total monoterpenes in the atmosphere¹¹. Thus, accurate models predicting the distribution and formation of SOA in the atmosphere require information on both speciated and total monoterpene fluxes.

Research Site

The measurement site is located on the western slope of the Sierra Nevada mountains near the Blodgett Forest Research Station¹². The site is a typical clear-cut plot, owned by Sierra Pacific Industries, planted with ponderosa pine (*Pinus ponderosa*) in 1990. Rainfall at the site occurs predominantly between September and May, with little rainfall during the summer months, characteristic of a Mediterranean-type climate. The predominant daytime airmass trajectory is directed upslope from the Sacramento Valley, providing regular transport of polluted air to the site. At night, the air flows downslope from the Sierra Nevada mountains, bringing cleaner air to the site that is representative of northern midlatitude background concentrations. A walk-up tower was erected in 1997, and currently supports meteorological and trace gas instrumentation for measurements of mixing ratios and fluxes of CO₂, H₂O, O₃, and a wide suite of VOCs^{12,13,14,15}.

Speciated Terpene Measurements

At our site, fluxes of monoterpenes and other VOCs are measured using a dual channel gas chromatograph with flame ionization detectors (GC-FID) coupled with relaxed eddy accumulation (REA)^{14,15}. The REA technique¹⁶ involves differential sampling, at a constant flow rate, of air into updraft and downdraft reservoirs based on the sign of the vertical wind speed, as determined by a sonic anemometer located on our measurement tower. Fluxes are calculated by:

$$F = b\sigma_w(C_u - C_d) \quad (1)$$

where b is a proportionality constant determined from measurements of sensible heat flux and temperature, σ_w is the standard deviation of the vertical wind speed, and C_u and C_d are the VOC mixing ratios in the up and downdraft reservoirs. Up and downdrafts are sub-sampled from within the main sample stream and separated with Teflon segregator valves when the vertical wind speed (w) exceeds a deadband of $0.6\sigma_w$, using a 5 min average of w and σ_w .

The two separate sub-samples are pre-concentrated onto a pair of Silcosteel microtraps, sequentially filled with approximately equal amounts (~12mg) of Carbopack B and Carbosieve SIII trapping material. The traps are embedded in a cold block, kept at ~ -10°C during sampling. After collection, samples are thermally desorbed (250°C for 1.2 min) on a pair of Rtx-WAX columns, and detected by dual FIDs. The setup is fully automated and measures a pair of 30 min average samples once every hour¹⁵.

The dominant monoterpene species emitted at our site are α -pinene, β -pinene, 3-carene, and limonene, with myrcene, β -phellandrene, camphene, and sabinene tentatively identified or expected to be present at our site. Monoterpene emissions are temperature dependent¹⁷ whereas mixing ratios exhibit a strong diurnal trend with concentrations highest in the evening when the nighttime boundary layer prevents vertical mixing of air (see Figure 1).

Blodgett Forest, CA: Sept 2000

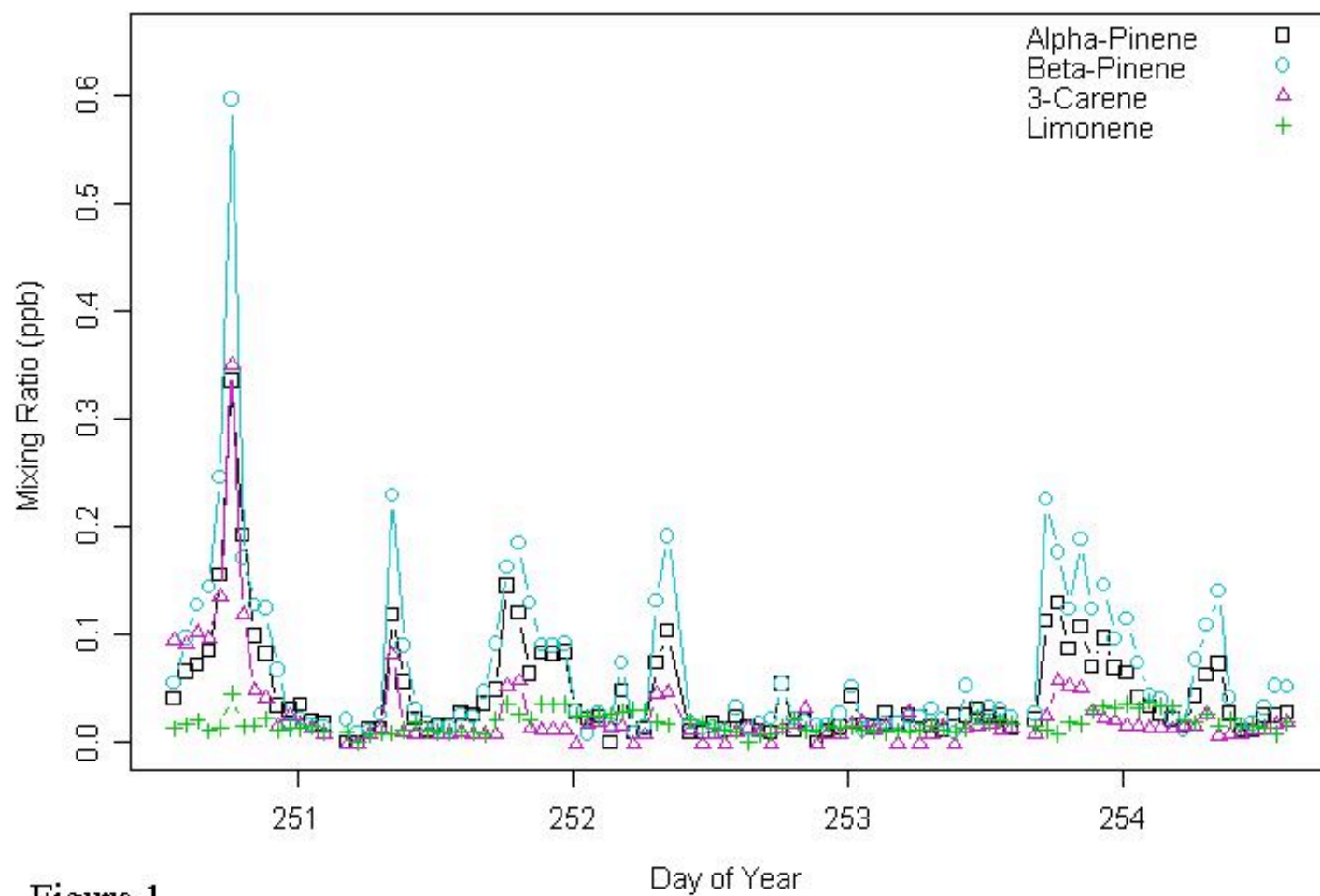


Figure 1

Preliminary SOA Production Models

A data set consisting of monoterpene mixing ratios and meteorological data from September 2000 was used for preliminary estimates of SOA formation at our site resulting from the oxidation of monoterpenes. Many numerical models predicting SOA yield from monoterpene oxidation have been constructed, which typically either fit experimentally-determined SOA yields to mathematical equations describing gas-particle partitioning to obtain partitioning coefficients^{6,18,19}, or combine mechanistic considerations of monoterpene oxidation to smog chamber results^{20,21,22}. As a first step in estimating SOA formation, a simple parameterized two-product yield model was used, whereby SOA yield is described by:

$$Y = M_0 * \frac{\alpha_i K_i}{1 + K_i M_0} \quad (2)$$

where Y is the SOA yield from monoterpene oxidation, M_0 is the initial organic aerosol concentration, α_i is a stoichiometric factor relating the total amount of product i formed to the total amount of monoterpene reacts, and K_i is the equilibrium coefficient representing the fraction of product i that partitions to the aerosol phase¹⁸. The α and K values for α - and β -pinene, 3-carene, and limonene suggested by Griffin et al.¹⁹ were used to determine both SOA yield, and total SOA concentration, which is calculated from Yield * Total amount of monoterpene reacted. In this preliminary analysis, the initial organic aerosol concentration is assumed to be $5\mu\text{g}/\text{m}^3$. The parameter values suggested by Griffin et al.¹⁹ result from smog chamber studies that involve monoterpene oxidation by OH and O_3 , but not by the nitrate radical. Additionally, the equilibrium coefficient, K , is highly temperature dependent, which may affect the applicability of smog chamber results obtained at elevated temperatures, to ambient environmental conditions. Thus, an equation to correct the value of K for temperature²², was also applied in this analysis.

Total SOA Formation from Main Terpene Species

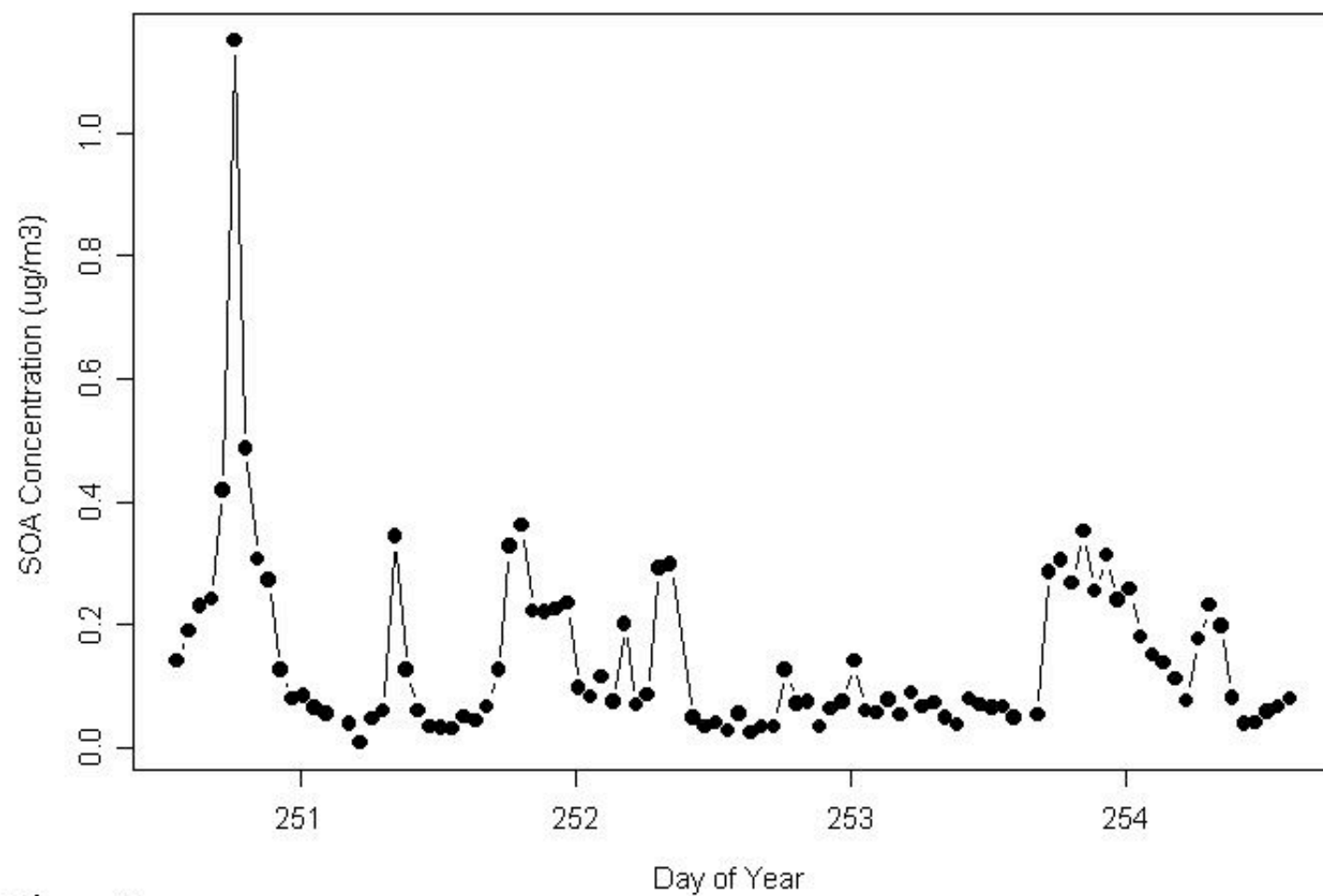


Figure 2

Model Results (Griffin et al. 1999) for SOA Concentration: Sept 2000

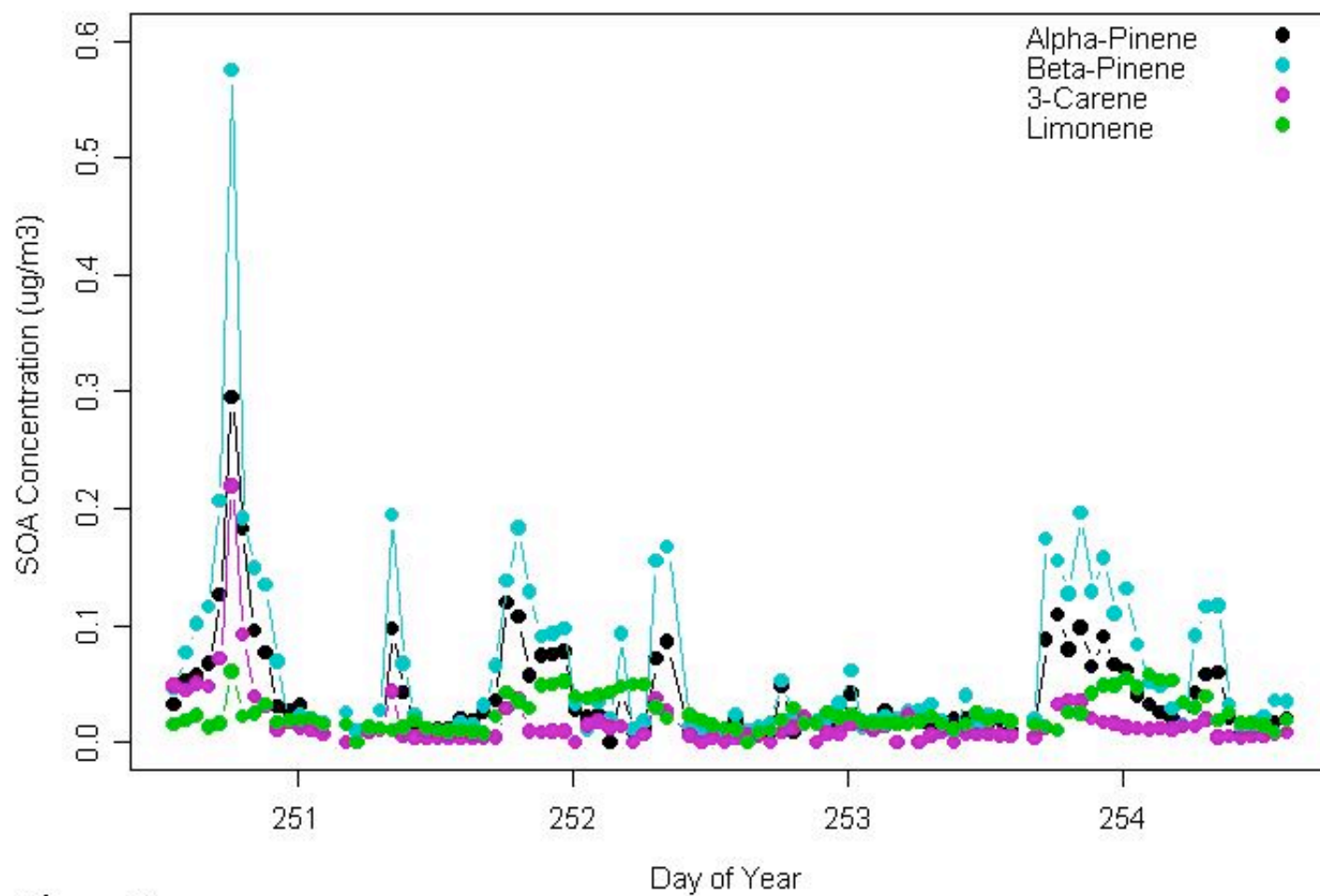


Figure 3

Model Results (Griffin et al. 1999) for Sept 2000

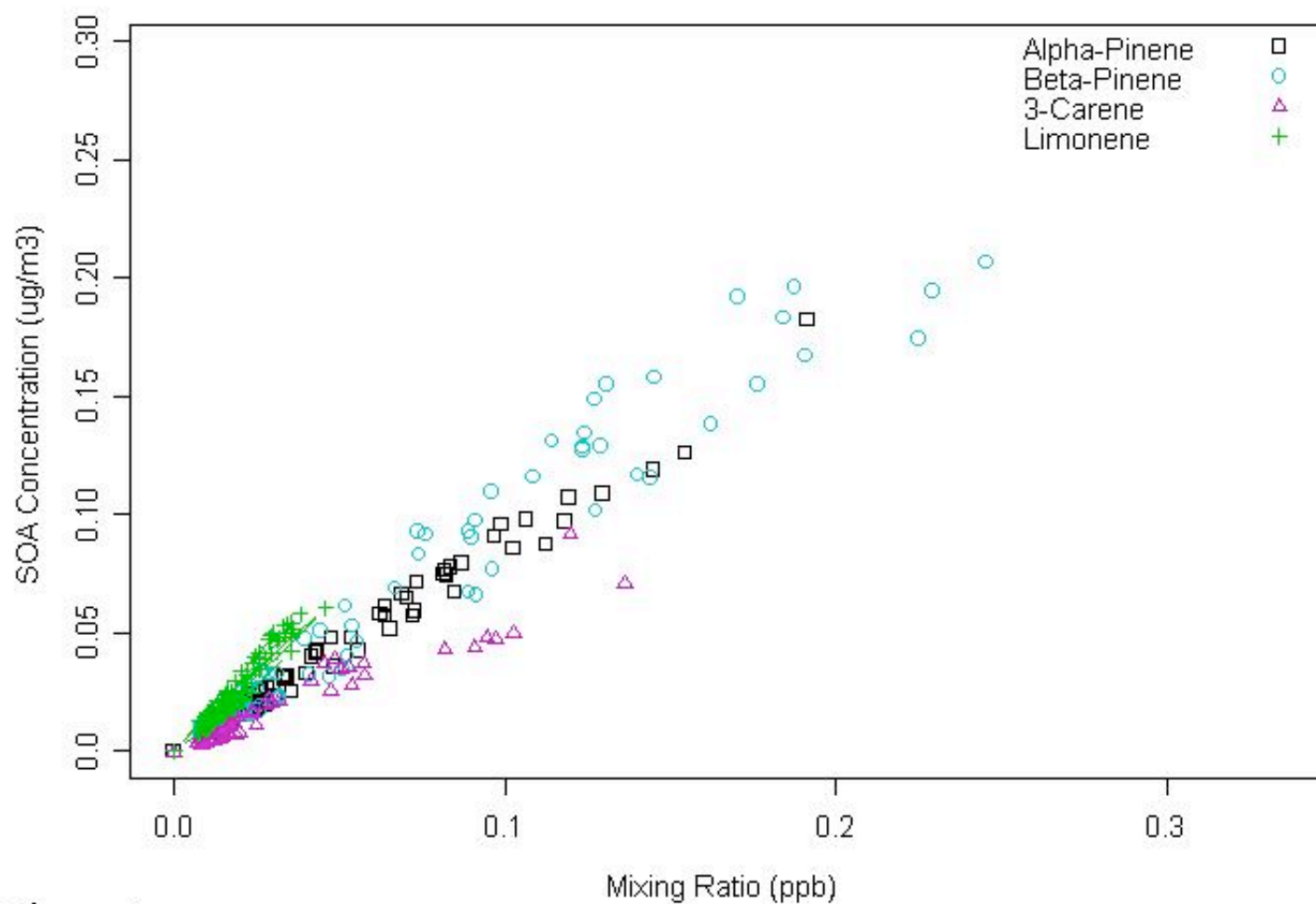


Figure 4

Model Results (Griffin et al. 1999) for SOA Yield: Sept. 2000

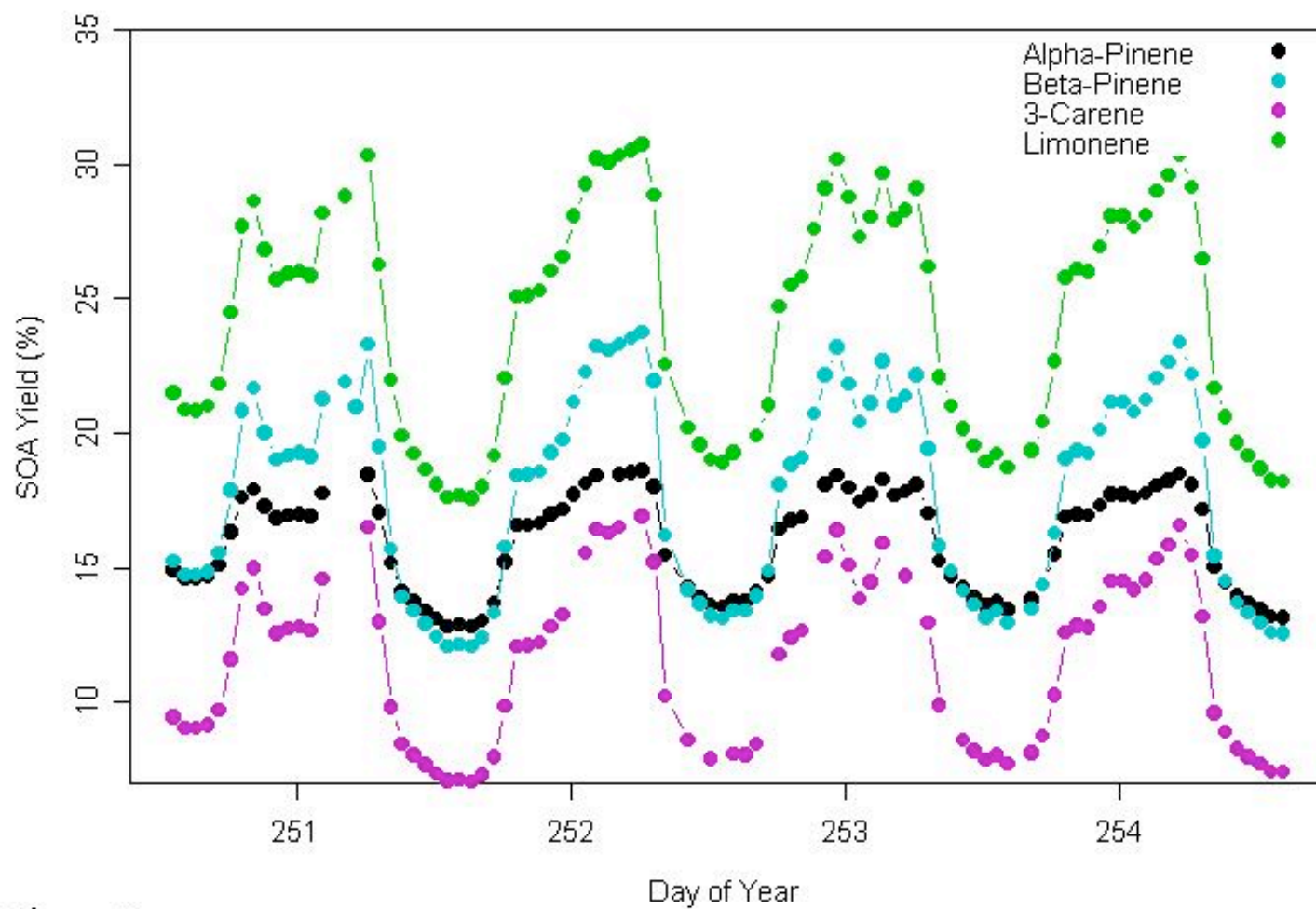


Figure 5

Model Results (Griffin et al. 1999) for SOA Yield: Sept. 2000

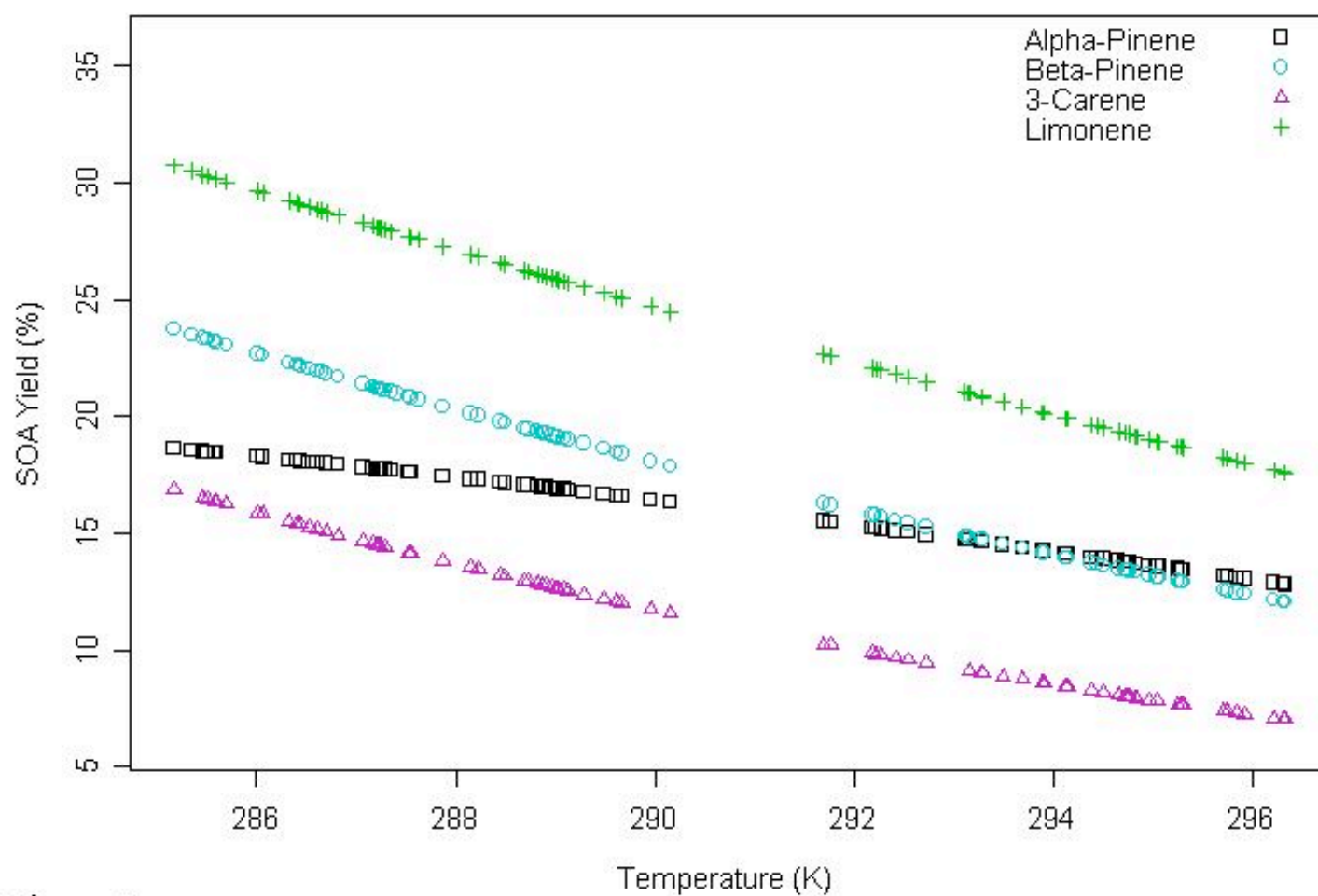


Figure 6

Results of SOA Model

- Total SOA concentrations range from near 0 to $\sim 1 \mu\text{g}/\text{m}^3$, averaging $\sim 0.3 \mu\text{g}/\text{m}^3$ (Figure 2)
- Concentration of total SOA is dominated by SOA formed from β -pinene and α -pinene (Figure 3)
- SOA concentration is strongly dependent on the initial concentration of monoterpene, as suggested by Eq 2 (Figure 4)
- Limonene is more responsive to changes in initial concentration than the other three terpene species (Figure 4)
- Limonene has the highest SOA yield (amount of SOA produced from the amount of monoterpene reacted), followed by β -pinene, α -pinene, and 3-carene (Figure 5)
- SOA yield is strongly temperature dependent, with highest yields when temperatures are lowest (Figure 6)

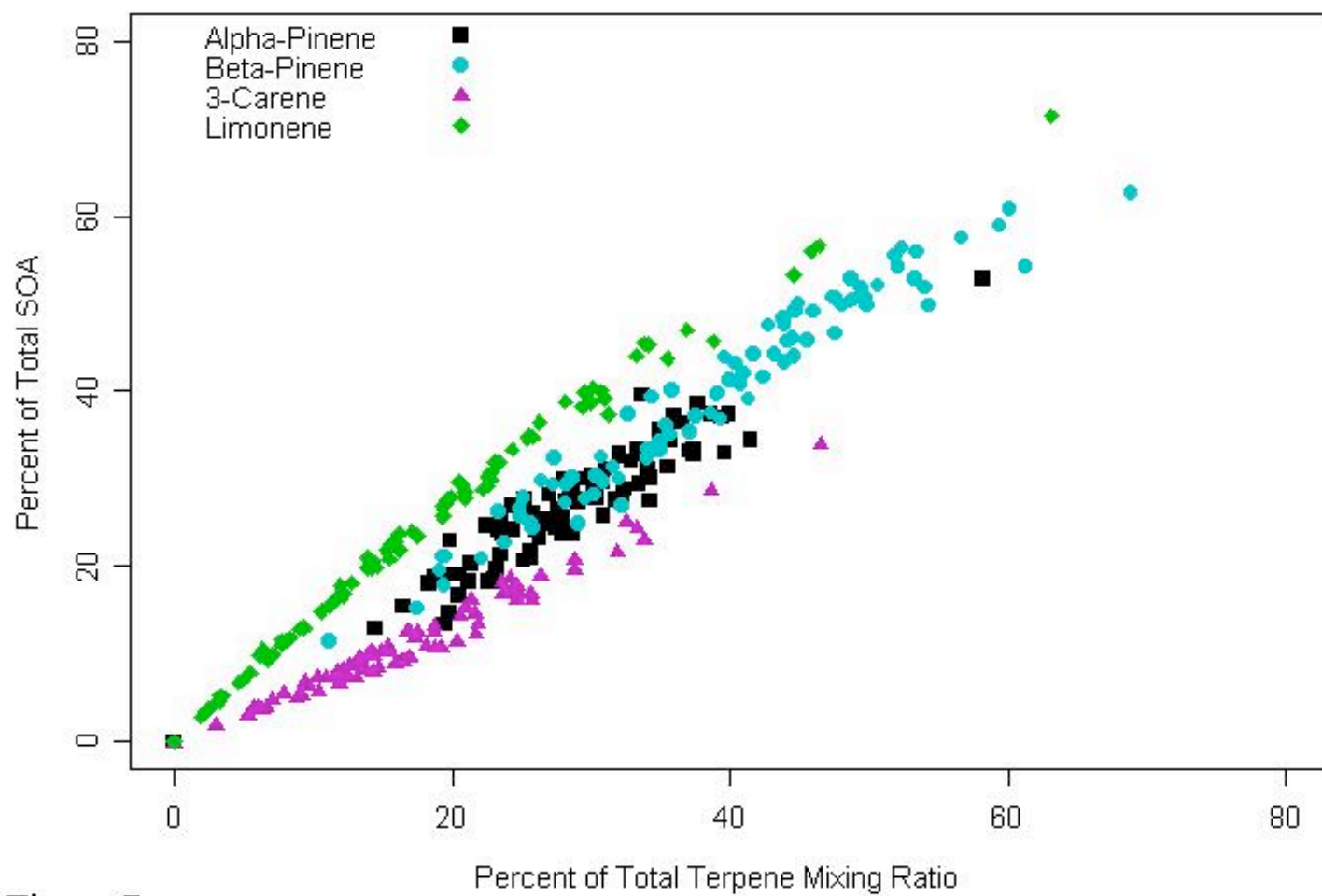


Figure 7

Discussion

- Monoterpene species that are not dominant contributors to total terpene mixing ratios, such as limonene, may still contribute significantly to total SOA concentration (Figure 7)
- Oxidation of limonene, with two C-C double bonds, resulted in higher SOA yields than oxidation of α -pinene, β -pinene, and 3-carene, all with one C-C double bond
- This suggests that monoterpenes with two or more C-C double bonds, such as limonene, myrcene, phellandrene, terpinene, and terpinolene may be important contributors to SOA formation, and that high SOA production would be expected when mixing ratios of these species are elevated in comparison to our site
- SOA concentrations calculated here are based on *instantaneous* partitioning of terpene mixing ratios, not rates of SOA production
⇒ Next step should use terpene emission rates to calculate SOA production rates

Critiques of Current Model

- Numerous assumptions were made in the current analysis, and can be improved in many ways, such as using simultaneous in situ measurements of organic aerosol concentration, considering monoterpene emission rates rather than instantaneous mixing ratios, and including the dependence of PAR and oxidant concentrations on monoterpene oxidation and SOA formation
- Despite correcting for the effects of temperature on K, applying parameter values fit to smog chamber results may be problematic due to additional factors, such as differences in relative humidity, elevated terpene and oxidant mixing ratios, nighttime presence of NO_3 , seasonal and latitudinal variations in photon flux density, and high seed aerosol concentrations, which suggests the need for more mechanistic based models

Upcoming Research

Because measurements of a limited number of speciated monoterpenes may not accurately represent the impact of total terpenes to the atmosphere, our future research will involve measurements of total monoterpenes as well as terpene oxidation products in the gas and aerosol phases, using a Proton Transfer Reaction-Mass Spectrometer (PTR-MS). Funding for the acquisition for the PTR-MS has been granted recently by the National Science Foundation. These measurements will provide key in situ observations of total and speciated monoterpenes and their gas and aerosol phase oxidation products to evaluate, and hopefully improve upon current models of SOA formation.

Monoterpene mixing ratios from data sets compiled over several years at our site will also be applied to mechanistic models of SOA production to understand seasonal trends in SOA production and to compare mechanistic models and models based on smog chamber yields with field measurements terpene oxidation products in the gas and aerosol phase.

Conclusions

- Monoterpenes that are more reactive (and thus harder to measure, and harder to study) with two or more C-C double bonds may be important contributors to SOA production
- Many adjustments must be made in order to address the numerous assumptions and refine this very preliminary analysis of SOA formation at our site
- A longer data set of both total and speciated monoterpene mixing ratios is required to elucidate any seasonal or interannual trends in SOA formation and compare simple and the more complex mechanistic models with field measurements by PTR-MS
- Monoterpenes and secondary organic aerosols formed from monoterpene oxidation may play an important role not only on a global scale, affecting the radiation budget, but also on a regional scale, affecting air quality and human respiratory health

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